

DIRECT ATMOSPHERIC EVIDENCE FOR THE IRREVERSIBLE FORMATION OF AQUEOUS SECONDARY ORGANIC AEROSOL (aqSOA)

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This study characterizes the reversible nature of aqSOA formation through direct atmospheric observations. Water-soluble organic carbon in the gas- and particle phases (WSOC_g and WSOC_p) was measured simultaneously to quantify aqSOA formation in Baltimore, MD, a site heavily impacted by anthropogenic and biogenic emissions. Daytime data show strong photochemical production of both WSOC_p and WSOC_g, as their normalized concentrations approximately doubled from 08:00 to 14:00 (local time). During the night, the fraction of total WSOC in the particle phase [$F_p = \text{WSOC}_p / (\text{WSOC}_p + \text{WSOC}_g)$] showed a pronounced increase with increasing relative humidity (RH), as the median F_p at the highest RH levels (> 80%), increased by approximately 50% compared to the median nighttime F_p at the lowest RH levels. This provides evidence for aqSOA formation, as the WSOC_g increasingly partitioned to the particle phase with increasing RH due to the enhanced aerosol liquid water content. To characterize the reversible/irreversible nature of this aqSOA, the WSOC_p measurement was alternated through an unperturbed ambient channel and through a ‘dried’ channel maintained at ~40% RH (with 7-s residence time) to mimic the natural drying that particles may undergo over the course of a day. We focus on comparing the behavior of WSOC_p in dried/ambient particles under the two predominant SOA formation regimes: 1) daytime photochemical SOA production, and 2) nighttime partitioning of WSOC_g to particle phase (WSOC_p) at enhanced RH (i.e., aqSOA formation). Across the entire RH range encountered, there was no statistically-significant difference in the WSOC_p concentrations through the dry and ambient channels, indicating that the aqSOA remained in the condensed phase upon the evaporation of aerosol water. This strongly suggests that the observed aqSOA was formed irreversibly. The results also indicate that the evaporation of aerosol water did not impact SOA formed through gas-phase oxidation pathways. This represents, to our knowledge, the first attempt to quantify and differentiate reversible and irreversible aqSOA in the atmosphere. These results have implications for interpreting laboratory and modeling studies of aqSOA.